10/524003

3/PRTS

DT05 Rec'd PCT/PTO 08 FEB 2005

CONTAINER FOR STORING AND TRANSPORTING LIQUID CHEMICAL AGENT

FIELD OF THE INVENTION

The present invention relates to a liquid chemical storage and/or transport container. More particularly, the present invention relates to a storage and/or transport container for chemical liquids for electronic materials, for example, photoresist compositions, particularly chemical liquids sensitive to temperatures, such as photosensitive antireflection coating compositions, rinsing liquids, developing solutions, stripping liquids, etching liquids, solvents and the like.

BACKGROUND ART

In production plants, in transporting a chemical liquid for an electronic material such as photoresist, it is common practice to fill the chemical liquid, for example, into a glass bottle or a plastic container formed of polyethylene, polypropylene or the like. In recent years, however, a method is adopted wherein, in transporting a chemical liquid for an electronic material, a plastic bag is placed in a stainless steel container and the chemical liquid for an electronic material is filled into the plastic bag. For some types of chemical liquids, a tank lorry or truck is used for the transport. Japanese Patent Publication No. 99000/1994 discloses a container which uses a disposable film pouch within a bottle or an overpack, and, for example, Japanese Patent Laid-Open Nos. 292933/1999, 95565/1997, and 153865/2000 disclose plastic containers which can prevent contamination with impurities and are suitable, for storage, for example of highly pure chemical liquids.

Among chemical liquids for electronic materials are included those which require temperature control for stable chemical liquid storage purposes or the like. In

particular, for example, photoresist compositions, when stored at room temperature, disadvantageously cause a change in sensitivity. Therefore, in this case, temperature control is indispensable for maintaining the quality of the photoresist compositions. In these chemical liquids, it is common practice to fill the chemical liquid into a glass or plastic container before storage or transport, with temperature control, of the chemical liquid together with the container. In this case, for storage of the chemical liquid together with the container, a cold room is necessary, and, for transport, the use of a cold insulator or a refrigerator truck is necessary. Further, not a few chemical liquids for electronic materials contain compounds which are designated as hazardous materials, for example, in the Fire Services Act. Therefore, in many cases, a cold reserving warehouse for hazardous materials is necessary for storage of the chemical liquids. Thus, the conventional container is inconvenient in handling at the time of storage or transport and further incurs increased facility cost for storage or transport. This had led to a demand for a container which is more convenient, can be safely handled and can stably store a chemical liquid.

In the liquid chemical storage and/or transport container according to the present invention, a Peltier element may be used as a temperature controller. Inventions directed to applications or use of the Peltier element which are different from those in the present invention are disclosed in the following publications.

Specifically, Japanese Patent Laid-Open No. 218862/2002 discloses a low-temperature water tank for live fish transportation which can transport live fishes using a simple small-sized container while keeping their lives. In this low-temperature water tank, a heat conduction plate to be cooled down by the Peltier

element is immersed in water in the container, and the temperature is dropped to make the live fishes in a torpid state in water and thus to retain their freshness.

Japanese Patent Laid-Open No. 192719/1998 discloses a device which can load or unload plural sample bottles into and from a sample thermostat at the same time. In this device, a Peltier element is equipped in contact with a metallic material constituting the bottom face of the device and functions to regulate the temperature of a sample.

Domestic Re-publication of PCT International Publication No. 67893/2000 discloses a chemical reactor capable of enhancing the rate of chemical reaction within a reaction pool. The reactor comprises a substrate with a reaction pool formed in its surface, a high-thermal-conductivity diamond layer forming the bottom of the reaction pool, a Peltier element attached on the back of the thermal conductive layer, and temperature control means for controlling the Peltier element to periodically change the temperature of the buffer in the reaction pool. The object of the invention described in this publication is to periodically change the temperature in the chemical reaction.

Japanese Patent Laid-Open No. 83077/1999 discloses a fluid temperature/humidity controller. In this fluid temperature/humidity controller, a fluid which an object of controlling is dehumidified to bring the humidity of the fluid to a particular value. This fluid is pre-cooled with cooling water to a first temperature and is then cooled by a Peltier cooler to a second temperature. The claimed advantage of this controller is that dehumidification and temperature control can be carried out with high accuracy and, at the same time, the energy efficiency as the whole device can be enhanced.

In all the above publications, there is a description to the effect that a Peltier element is used as temperature control means. None of them, however,

describes the use of the Peltier element as cooling means for a container for the liquid chemical storage and/or transport according to the present invention.

SUMMARY OF THE INVENTION

Under the above circumstances, the present invention has been made, and an object of the present invention is to provide a container which can stably store or transport a liquid chemical, such as a chemical liquid for an electronic material, without causing decomposition and sedimentation of the liquid chemical filled thereinto upon a change in temperature.

As a result of extensive and intensive studies, the present inventors have found that the above object can be attained by a container having a double structure comprising an outer cylinder and an inner cylinder, wherein a space defined by the outer cylinder and the inner cylinder is substantially vacuum or packed with a heat insulating material. The present inventors have further found that the provision of a temperature control function, for example, a Peltier element, in the container per se can realize stable storage of a chemical liquid for a longer period of time. The present invention has been made based on such finding.

Thus, according to the present invention, there is provided a liquid chemical container characterized by having a double structure comprising an outer cylinder and an inner cylinder, a space defined by the outer cylinder and the inner cylinder being substantially vacuum or packed with a heat insulating material.

EFFECT OF THE INVENTION

The use of the liquid chemical container according to the present invention can realize storage and/or transport of liquid chemicals, particularly chemical liquids for electronic materials, for example, photoresists, rinsing liquids, developing solutions,

stripping liquids, etching liquids, and solvents, at an appropriate temperature or at a low temperature with the aid of a temperature controller, can prevent a deterioration in properties upon a change in temperature of the chemical liquid filled into the container, and can maintain the quality of the chemical liquid.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a sectional broken side view of a principal part of a liquid chemical container according to the present invention and Fig. 1B is a sectional top view of the liquid chemical container shown in Fig. 1A; and

Figs. 2 to 5 are cross-sectional views of liquid chemical containers according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the structure of the container according to the present invention are shown in Figs. 1 to 5.

An embodiment of the present invention will be described with reference to Fig. 1.

The container of the present invention shown in Fig. 1 has a double structure comprising an outer cylinder 11 and an inner cylinder 12. Materials usable for the outer cylinder and the inner cylinder constituting the container include materials, which can be molded to containers, for example, metals such as stainless steel, iron, and brass, or plastics such as polyethylene, polypropylene, and fluororesins. Among them, metals are preferred from the viewpoint of good resistance to external physical stress. Further, the use of plastic materials is preferred from viewpoints of their low chemical reactivity with a chemical liquid filled into the container and, in its turn, less susceptibility of impurities to dissolution in the chemical liquid. In the container, the material for the outer cylinder is not

necessarily required to be the same as that for the inner cylinder, and the material for the outer cylinder and the material for the inner cylinder may be selected depending upon applications of the container.

For the inner cylinder, a suitable material should be selected depending upon the type of the chemical liquid to be filled into the inner cylinder. Specifically, the inner cylinder, which comes into direct contact with the chemical liquid filled thereinto, is preferably not reactive with the chemical liquid and further is preferably formed of a material which does not dissolve in the chemical liquid. Specific examples of preferred materials for the inner cylinder include fluororesins and SUS 306. Further, as described later, when a temperature control member is provided, on the outer side of the inner cylinder, in contact with the inner cylinder, or when a Peltier element is mounted on the outer side of the container opening in the inner cylinder, preferably, the inner cylinder is formed of a material having high thermal conductivity from the viewpoint of improving the efficiency of heat exchange between the temperature control member and the chemical liquid filled into the container. Materials satisfying this requirement include metallic materials. In general, however, metallic materials are likely to be dissolved in chemical liquids or are likely to be reacted with chemical liquids. Therefore, in order to provide a combination of good thermal conductivity with good resistance to chemical liquids, coating of resins having high chemical resistance onto the inner cylinder in its surface, which comes into contact with the chemical liquid, is also preferred. In particular, when a chemical liquid for an electronic material is filled into the inner cylinder, dissolution of a metal in the chemical liquid sometimes results in a significant deterioration in the properties of the chemical liquid. Therefore, the structure of the inner cylinder is

preferably such that the chemical liquid does not come into contact with a material which is likely to cause a metal to be dissolved in the chemical liquid.

On the other hand, the outer cylinder preferably has high resistance to impact or the like which the outer cylinder undergoes at the time of transport or the like. From the viewpoint of heat retaining properties, preferably, the outer cylinder is formed of a material having low thermal conductivity.

In the container of the present invention shown in Fig. 1, a space 13 defined by the outer cylinder 11 and the inner cylinder 12 is hermetically sealed. The space 13 is substantially vacuum. The expression "substantially vacuum" as used herein means that the degree of vacuum is, for example, not more than 100 Pa, preferably not more than 1 Pa, more preferably not more than 0.01 Pa. However, the degree of vacuum required varies depending upon heat insulation effectiveness required of the container.

If necessary, the container according to the present invention is stoppered with a lid member (not shown in the diagrams). In the present invention, by virtue of the above construction, temperature exchange between the chemical liquid within the container and the exterior of the container can be suppressed, and the heat insulation of the chemical liquid within the container can be ensured. More preferably, the container is provided with a temperature controller 14 as shown in Fig. 1.

The temperature controller 14 is not particularly limited so far as it can set the temperature of a chemical liquid filled into the container to a value useful for the storage of the chemical liquid. When the chemical liquid to be filled into the container is a photoresist composition or the like, a conventional device, which is commonly used in the storage of this type of chemical liquid and can control the temperature

in the range of about −20 to 10°C, may be used. In the temperature controller 14 shown in Fig. 1, a coolant is circulated through temperature control piping 15 to regulate the temperature of the chemical liquid filled into the inner cylinder 12.

Coolants usable in the temperature controller include, for example, hydrochlorofluorocarbon compounds such as HCFC-22, HCFC-123, HCFC-141b, HCFC-142b, and HCFC-225, hydrofluorocarbon compounds such as HFC-32, HFC-125, HFC-134a, HFC-143a, and HFC-152a, and ammonia. Among them, hydrofluorocarbon compounds are preferred from the viewpoint of environmental problems. That is, advantageously, hydrofluorocarbon compounds are not ozone layer destructing substances and, at the same time, are nontoxic and noncombustible.

In the container shown in Fig. 1, if necessary, the piping for the circulation of a coolant is provided with valves 16a, 16b for separation from the container. When the container has a relatively small capacity, for example, a capacity of 50 to 500 liters, the container body can be separated from the temperature controller so that only the container body can be independently transported or stored. In the container according to the present invention, heat insulation effect can be attained without the provision of the temperature controller. Therefore, the temperature controller can be separated from the container body. When the container body is separable from the temperature controller, the temperature controller can be used in common to a plurality of containers. This is also advantageously cost effective.

Fig. 2 shows another embodiment of the present invention. According to this embodiment, in a container comprising an outer cylinder and an inner cylinder, a temperature controller is mounted on the outer side of the outer cylinder of the container integrally with the container. In the case of a container having a

relatively large capacity, for example, a capacity of about 1 m^3, as shown in Fig. 2, the liquid chemical filled into the container can also be transported and stored in such a state that the temperature controller 14 has been equipped integrally with the container body. In the container shown in Fig. 2, the piping 15 for temperature control is in direct contact with the chemical liquid filled into the container. At that time, preferably, the temperature control piping per se or the outer surface of the temperature control piping is formed of a material which is not reactive or is less likely to be reacted with the filled chemical liquid.

In embodiments of the container according to the present invention shown in Figs. 3 and 4, temperature control piping 15 has been inserted through an opening in the container. The temperature control piping can be inserted integrally with a lid of the container. When this structure is adopted in the container, the container can be manufactured in a simpler manner.

In the embodiment shown in Fig. 3, a heat insulating material 31 is inserted into a space defined by an outer cylinder 11 and an inner cylinder 12. The heat insulating material to be packed into the space between the inner cylinder and the outer cylinder is not particularly limited so far as the material has heat insulating effect. Examples of heat insulating materials usable herein include glass wool, rock wool, calcium silicate, pearlite, expanded polystyrene, rigid polyurethane, flexible polyurethane, polyethylene, phenol foam, and polystyrene foam. When these heat insulating materials are used, the space between the outer cylinder and the inner cylinder is not necessarily required to be hermetically sealed.

In the embodiment shown in Fig. 4, the space defined by the outer cylinder and the inner cylinder is substantially vacuum. In this embodiment, since temperature control piping is introduced through an

opening in the container, there is no need to use a heat conductive material in the inner cylinder. Therefore, the freedom in design can be ensured.

In the embodiment shown in Fig. 5, a device 14, which can electrically control the temperature, for example, a Peltier element, is additionally provided in the inner cylinder in its container opening part. The Peltier element comprises dissimilar conductors joined to each other and utilizes Peltier effect which is such a phenomenon that, when current is allowed to flow through the junction between the dissimilar conductors, a temperature difference occurs. The Peliter element has recently become utilized in various refrigerating devices and temperature controllers.

In the device shown in Fig. 5, the temperature controller 14 is driven by a battery 51. When a device which can electrically control the temperature, such as a Peltier element, is used, power is easily available from a power supply of a warehouse or a battery of a transport vehicle. Therefore, at the time of transport and storage, the temperature of the liquid stored in the container can be easily controlled.

The shape of the container, and the shape, arrangement, position, etc. of temperature control piping through which a coolant for temperature control is passed, are not limited to those in the above embodiments and may be varied depending upon other conditions.

EXAMPLES

The following examples further illustrate the present invention. However, it should be noted that embodiments of the present invention are not limited to these examples only.

Examples 1 and 2

A positive-working photoresist AZ 1350 manufactured by Clariant Japan K.K. was filled into a container shown

in Fig. 1 and a container shown in Fig. 5 and was stored in the containers with the preset internal temperature (preset temperature of contents) of the container being 5°C. For the photoresist, the sensitivity and the number of fine particles having a size of not more than 0.5 μm in the resist were measured by the following methods immediately after the filling and one month, three months and six months after the filling. The results were as shown in Tables 1 and 2.

Sensitivity

AZ 1350 manufactured by Clariant Japan was spin coated onto a 4-in. silicon wafer. The coating was baked on a hot plate at 100°C for 90 sec to prepare a 1.5 μm-thick resist film. This resist film was subjected to 1 mm-square punched pattern exposure by means of a g line stepper (DSW 6300, manufactured by GCA), followed by development with a 2.38 wt% aqueous tetramethylammonium hydroxide solution at 23°C for 60 sec to form a punched pattern. Thereafter, observation under a microscope was carried out to determine minimum exposure necessary for removing the resist film. This exposure was designated as optimal exposure. Further, the rate of change in sensitivity was calculated by the equation (initial sensitivity - sensitivity X months after the measurement of the initial sensitivity)/initial sensitivity.

In general, the sensitivity of the resist shifts toward higher sensitivity over time, because the photoactive compound is decomposed with the elapse of time to cause lowered dissolution inhibitory action which increases the sensitivity.

Number of fine particles

The number of fine particles in AZ 1350 manufactured by Clariant Japan K.K. was measured with a particle counter KL-20A manufactured by RION Co., Ltd.

Comparative Examples

In order to examine the influence of the internal temperature of the container on the sensitivity of the

resist and on the number of fine particles produced during the storage of the resist, the procedure of Example 1 was repeated, except that the internal temperature of the container was kept at room temperature (23°C, Comparative Example 1) and 40°C (Comparative Example 2). The results were as shown in Tables 1 and 2.

Table 1
Rate of change in sensitivity

	Temp., °C	Start	After 1 month	After 3 months	After 6 months
Ex. 1	5	0	0.1	0.3	0.3
Ex. 2	5	0	0.2	0.3	0.3
Comp.Ex. 1	23	0	0.5	0.8	1.6
Comp.Ex. 2	40	0	3.2	5.1	12.6

Table 2
Change in number of fine particles

	Temp., °C	Start	After 1 month	After 3 months	After 6 months
Ex. 1	5	1	3	2	2
Ex. 2	5	2	2	3	2
Comp.Ex. 1	23	1	10	23	43
Comp.Ex. 2	40	1	153	589	> 1000

Example 3

A container shown in Fig. 5 was provided for measuring its heat insulating property. The container shown in Fig. 5 was provided with a Peltier element as a device which can electrically control the temperature. In such an environment the ambient temperature was kept at about 23°C, water of 5.0°C was filled into the container. The Peltier element was energized for temperature control. The temperature of the contents of the container was measured over time. The results were as shown in Table 3. From the results shown in Table 3, it is apparent that when the container shown in Fig. 5 was used, the temperature of the contents of the

container can be maintained without a substantial temperature change.

Table 3
Heat insulation test

Time, hour	0	2	4	6	8	10
Ambient temp., °C	22.4	23.0	23.1	23.1	23.0	23.2
Temp. of contents, °C	5.0	5.1	5.6	6.0	6.3	6.3